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(54) Title: SOLUTIONS FOR STABILIZING HYDROGEN PEROXIDE CONTAINING SOLUTIONS (57) Abstract <p>Aqueous stabilizing solutions are provided for stabilizing hydrogen peroxide, comprising the following constituents: citric acid 1 to 7 mass percent/vol., tartaric acid 7 to 12 mass percent/vol. and a chelating and/or buffering agent. In one set of embodiments, the stabilizing solution may include silver ions in the concentration range 5 to 30 parts mass % by volume. Other embodiments of the invention are characterized by the substantial absence of silver. The stabilizing compositions may be used to stabilize hydrogen peroxide-containing composition useful as a disinfectant for water, e.g. as a swimming pool disinfectant.</p>		

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SOLUTIONS FOR STABILIZING HYDROGEN PEROXIDE CONTAINING SOLUTIONS

This invention relates to stabilising solutions for stabilising hydrogen peroxide, to stabilised hydrogen peroxide-containing biocidal compositions and to methods for using same. More specifically the invention provides a concentrate which is active as a stabilizer for hydrogen peroxide and to disinfectant solutions formed by mixing the concentrate and hydrogen peroxide.

Oxidizing agents are employed in large quantities in industry for disinfectant and sanitizing application. Thus chlorine and hypochlorite compounds are traditionally used for water treatment, such as potable water supplies and swimming pools, as well as for environmental cleansing operations and the treatment of food-producing and other equipment where hygienic conditions are paramount. Thus known procedures for maintaining desired bactericidal levels in water supplies, swimming pools and circulating baths of the "Jacuzzi" type generally rely upon the use of sources of chlorine or hypochlorite ions in order to eliminate viable pathogenic organisms. Other known procedures include exposing the water to ozone and circulating the water through irradiating zones where the water is exposed to high levels of UV radiation.

The use of chlorine and hypochlorite for treating water supplies has the disadvantage that chlorine escapes to the environment where it can have a pronounced polluting effect and organic compounds present in the water become chlorinated to produce toxic organo-chlorine compounds. The use of ozone and U.V. irradiation involves the use of expensive equipment and high running costs.

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Hydrogen peroxide is well known as an oxidizing agent and biocide and has found widespread application in limited fields such as, for example, the carbon in pulp process, in metallurgical recovery and to provide nascent oxygen.

Hydrogen peroxide has many advantages over chlorinating materials in disinfectant and sanitizing applications. For example, hydrogen peroxide is not a pollutant, decomposing to oxygen and water. It also does not react with ammonia, thus avoiding potential undesirable by-products and its use can be controlled to provide selective oxidation. Hydrogen peroxide does react efficiently with sulphur compounds in aqueous media removing noxious odours. Thus it oxidizes hydrogen sulphide to produce water and elemental sulphur. An indication of the efficiency of the product in this regard is the fact that H_2S present at a concentration of 1 ppm in water can be completely oxidized by about one quarter of the quantity required using suitable chlorination products. Hydrogen peroxide is also effective against a broad range of bacteria including some which have become resistant even to chlorine, such as Pseudomonas aeruginosa.

However hydrogen peroxide is unstable with respect to its decomposition into water and oxygen, this process being accelerated in the presence of catalysts which are numerous and varied. Examples of these catalysts include metal surfaces, metal oxides and even some soluble salts, for example those of iron and copper. Thus the decomposition process is accelerated in the presence of a range of metal ions, mainly iron, copper, vanadium, nickel, chromium and manganese. These metals can decompose hydrogen peroxide by catalytically controlled chain reactions. Some of the metals form stable complexes with the hydrogen peroxide.

Decomposition of hydrogen peroxide also occurs in the presence of organic material.

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Mechanisms for hydrogen peroxide decomposition include hydrogen ion abstraction, radical chain termination occurring by combination with solution ions or attack by radical scavengers such as aromatic amines. Homolytic and heterolytic bond cleavage also occurs.

The decomposition process is also affected by pH and the presence or otherwise of stabilizers.

Because of the tendency of hydrogen peroxide to decompose, non-stabilized hydrogen peroxide is of limited use for many disinfectant/antiseptic applications.

With this tendency to decompose, the shelf-life of hydrogen peroxide is short and even in situations where nascent oxygen is required, this is generally generated too quickly for efficient use thereof. In order to prolong the useful life of hydrogen peroxide, particularly in stock solutions thereof, so called "inhibitors", i.e. substances which inhibit the decomposition of hydrogen peroxide to oxygen and water, may be used. Known inhibitors include hippuric acid, acetanilide and also phosphoric acid. However all of these are associated with various disadvantages such as limited effectiveness, high cost, non-degradability and odour.

A further use of hydrogen peroxide (as an aqueous solution) is as an antiseptic. This use, which relies upon the strong bactericidal properties of hydrogen peroxide, has also been limited because of the tendency of hydrogen peroxide to become deactivated by organic materials.

The patent literature discloses many examples of hydrogen peroxide stabilizers, most of which have little effect on hydrogen peroxide stability per se but appear to act rather as inhibitors of decomposition catalysts of the kind described above. Thus various complexing organic compounds have been suggested as sequestering or chelating agents.

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In EP 0209228 it has been proposed to form stabilized solutions of hydrogen peroxide by the addition of aminophosphonate chelating and aromatic amine free radical scavenging agents. This patent also proposes, inter alia, the use of a surfactant for control of the physical qualities of the stabilized hydrogen peroxide solution.

It is also known from the literature that non-stabilized 35% hydrogen peroxide is most stable in the pH range 2.5 to 4.5. At pH 3 the decomposition rate per day at 100°C is extremely low but rises to 90% at pH 1. In GB-A-2 189 394 the use is described of an inorganic acid, such as phosphoric acid, together with an organic acid, such as citric or tartaric acid as sequestering and buffering agents to provide a stabilizer concentrate, a source of silver ions also being provided as a synergist, to give a stabilized hydrogen peroxide solution with activity as a disinfectant in the food industry and for water treatment.

Specifically GB-A-2 189 394 describes a concentrate which can be mixed with hydrogen peroxide for a disinfectant. According to GB-A-2 189 394, this concentrate is made by mixing a solution of an aqueous inorganic acid having a pH less than or equal to 1.6 in deionised water, at between 50 and 60°C with colloidal silver, a silver salt or silver salt complex. Tartaric and/or citric acids are stated to be suitable stabilisers for use in combination with the silver compounds. The specification states that the new agents described are suitable for numerous applications, including use in water disinfection for swimming pools and hot whirlpools. However this proposed use ignores the high expense of silver and also the fact that in the aforementioned uses, it is highly undesirable for silver containing compounds to be allowed to contact the polymer-based decorative surfaces (including plastics fittings, coloured rubber connectors and accessories and painted surfaces) which are inevitably present in swimming pools and other bathing facilities such as, for example,

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Jacuzzis. Accordingly, the compositions of GB-A-2 189 394 have failed to achieve acceptance for these uses.

The compositions of GB-A-2 189 394 further have been found to be less than satisfactory in fulfilling their prime objective of providing a satisfactory degree of longevity for hydrogen peroxide stock solutions. On investigation the reason for this appears to be the lack of appreciation that tartaric acid has an unexpectedly high stabilizing ability when used at relatively high concentrations in combination with citric acid. More specifically it has now been found that citric acid and tartaric acid, when present together in specific proportions wherein a relatively high concentration of tartaric acid is maintained have an enhanced and apparently synergistic stabilizing potential.

An object of the present invention is to avoid the aforementioned disadvantages and to provide a concentrate comprising phosphoric, citric and tartaric acids in specific proportions so that the concentrate has the property of stabilizing hydrogen peroxide solutions to provide a disinfectant which possesses sustained high activity even at extremely low concentrations.

According to one aspect of the invention there are provided aqueous stabilizing solutions for stabilizing hydrogen peroxide, comprising the following constituents

Citric acid	1 to 7 mass percent/vol.
Tartaric acid	7 to 12 mass percent/vol.

and a chelating and/or buffering agent. Preferably the chelating and/or buffering agent is present in a sufficient concentration to effect substantially complete chelation of metal ions capable of catalyzing the decomposition of hydrogen peroxide.

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Further according to the invention the chelating and/or buffering agent is preferably phosphoric acid and the citric, tartaric and phosphoric acids are provided in the ratio 1:4:2, the concentrations thereof being selected to provide a concentrate which has a pH between 1.5 and 3 and a maximum dissolved solids content of 38 000 ppm. As stated above non-stabilized hydrogen peroxide is most stable in the range 2.5 to 4.5 and a pH of the stabilizing solution in the stated range is effective suitably to buffer and enhance the stability of the stabilized product.

It has been found that a stabilizer concentrate solution incorporating the aforesaid constituents within the specified concentration ranges provides protection of a high order against decomposition of hydrogen peroxide and that disinfectant solutions formed therewith possess superior activity against pathogenic micro-organisms found, for example, in brewery installations.

In these embodiments, the stabilising solution may include silver ions in the concentration range 5 to 30 parts mass % by volume. The silver ions may be provided by means of a soluble silver salt, the silver providing for enhanced biocidal activity in the stabilized hydrogen peroxide solution, rendering the final solution efficacious in effluent treatment. The silver ions are preferably provided by a soluble silver salt such as at least one of silver nitrate, silver sulphate and silver nitrite, or by use of silver chloride. Where silver nitrate is used, the preferred ratio of the constituents silver nitrate to citric acid to tartaric acid to phosphoric acid is approximately 13:1:4:2.

The concentrate may be made simply by dissolving silver nitrate in de-ionised water and raising the temperature of the solution to approximately 30°C before adding the required amounts of citric and tartaric acid. This is followed by the phosphoric acid which is stirred into the solution for

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approximately one hour followed by an ultra-violet ray blocker if required, and the resulting solution may then be filtered through a 45µm millipore filter before use.

It will be appreciated that the stabilizing agents in the concentrate protect hydrogen peroxide against rapid decomposition, particularly in the presence of silver ions and that the silver ions act in synergy with the hydrogen peroxide to enhance the bactericidal properties of the disinfectant.

According to a further aspect of the invention, stabilizing compositions for stabilizing hydrogen peroxide have been devised which enable effective hydrogen peroxide-based biocidal compositions to be produced which do not rely upon the presence of silver.

According to this aspect of invention there are provided aqueous stabilizing solutions for stabilizing hydrogen peroxide, comprising the following constituents

Citric acid	1 to 7 weight percent
Tartaric acid	7 to 12 weight percent

and a chelating and/or buffering agent. Preferably the chelating and/or buffering agent is present in a sufficient concentration to effect substantially complete chelation of metal ions capable of catalyzing the decomposition of hydrogen peroxide, said compositions being further characterized by the substantial absence of silver.

Preferably in accordance with each aspect of the present invention, the chelating and/or buffering agent comprises phosphate ions which may be provided by incorporating phosphoric acid into the composition. The phosphoric acid is preferably provided in a concentration of from 2 to 6 weight percent. As above, the pH is preferably from 1.5-3.

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According to yet another aspect of the invention the concentrates provided according to each aspect of the invention incorporate an ultra-violet ray blocker, preferably acetanilide, to provide increased stability especially to highly diluted disinfectant solutions in high ultra-violet ray exposure conditions. Such ultra-violet blocker is added to the concentrate in the proportion of 0.02 to 0.1%.

A particularly preferred stabilizing composition according to the invention includes the aforementioned constituents in the following approximate preferred ratio:

Citric acid:tartaric acid:phosphoric acid = 1:4:2

Especially preferred stabilizing solutions have a maximum total dissolved solids content of 38000 ppm.

The invention further provides hydrogen peroxide-containing compositions stabilized by addition of the stabilizing compositions defined above. Such stabilized hydrogen peroxide solutions may be prepared by mixing aqueous hydrogen peroxide with the aforementioned stabilizing solutions in the following concentration ratios:

Hydrogen peroxide	99.7 to 97 mass percent/vol.
Stabilizing solution	0.25 to 3.0 mass percent/vol.

Preferably the concentrate is added to hydrogen peroxide by simple mixing in the range 1 to 99 to 1 to 199 of stabilizer concentrate to hydrogen peroxide. Such stabilized hydrogen peroxide disinfectant solutions have an extended shelf life and may be used for treatment of drinking water at 1 to 3⁴ ppm; in swimming pools at 50 to 100 ppm and for surface disinfection of equipment and the like at a concentration of 0.1 to 0.5%.

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Expressed in terms of mass percent/vol of the specified constituents the hydrogen peroxide-containing compositions according to the invention preferably comprise citric acid and tartaric acid in the following concentration ranges expressed as mass percent/vol aqueous H_2O_2 :

Citric acid	0.0025 - 0.21 weight percent
Tartaric acid	0.0175 - 0.36 weight percent.

Said hydrogen peroxide-containing composition according to one aspect of the invention are further characterized by the substantial absence of silver.

Also according to the invention a quaternary ammonium salt such as tetra-n-propyl ammonium hydrogen sulphate or other lipid soluble quaternary ammonium salt such as that sold under the trade name of BELLACIDE 350, is incorporated into the disinfectant solution. It is believed that such salt assists the transport of ions through the cell wall of bacteria thereby enhancing the biocidal activity of the product.

The said quaternary ammonium salt may be incorporated directly into the final made up hydrogen peroxide solution in concentration of 5 to 20%.

The quaternary ammonium salt, however, causes a reaction in the presence of silver ions giving rise to a precipitate and making it unsuitable for use in cases where silver has been added to the concentrate.

It has been found that when silver-containing stabilizing solutions are produced by the procedures described in GB-A-2 189 394 problems arise due to the formation of a yellow precipitate (believed to be silver phosphate) and as indicated above the biocidal potential of the resulting solutions is limited.

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There is further provided in accordance with the present invention, a novel process for producing the silver-containing aqueous stabilizing solutions according to the invention which avoids disadvantages of known procedures, particularly those described in GB-A-2 189 394.

According to this aspect of the present invention there is provided a method of producing a silver-containing stabilizing solution for stabilizing hydrogen peroxide which comprises the following steps carried out in the order specified:

- A. forming an aqueous solution comprising a water soluble silver salt at a temperature of from 20 to 40°C
- B. forming an aqueous solution comprising a water soluble silver salt, tartaric acid and citric acid from the solution formed in Step A
- C. forming an aqueous solution comprising a water soluble silver salt, tartaric acid, citric acid, and phosphoric acid from the solution formed in Step B

In carrying out Step B solid citric acid and tartaric acid may be dissolved in the solution formed in Step A. Alternatively, the citric acid and tartaric acids may be dissolved in water and the resulting solution mixed with the solution formed in Step A.

Step C may be carried out simply by mixing the solution from Step B with aqueous phosphoric acid.

The preferred ingredients and proportions thereof are as specified above with respect to the aqueous stabilizing solutions per se.

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As used herein the term "phosphoric acid" designates any of ortho-, metaand pyro- phosphoric acids and mixtures thereof. Preferably orthophosphoric acid is used.

The invention further provides the use of a hydrogen peroxide-containing composition as defined herein as a disinfectant for water, especially for a swimming pool. or Jacuzzi. Such use involves periodically adding a biocidally effective amount of a a hydrogen peroxide-containing composition as defined herein.

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The following examples illustrate the invention:

EXAMPLE 1

A stabilizing solution is provided for the stabilization of 50 volume hydrogen peroxide.

The stabilizing solution has the following composition and characteristics:

pH	2-3
total dissolved solids	38000
specific gravity	1.06
citric acid	2.10 mass %/vol
tartaric acid	8.00 mass %/vol
phosphoric acid	4.30 mass %/vol

The concentrate was made up by dissolving 80 gm of tartaric acid and 21 gm of citric acid in 500 ml de-ionised water at room temperature using a standard laboratory PYREX beaker suitably cleaned with de-ionised water. To this solution there was added 50 gm 85% orthophosphoric acid and the volume was made up to 1000 ml with de-ionised water and stirred for one hour until the solution was homogeneous. After filtration through a 45µm millipore filter the concentrate solution was added to 50 volume H₂O₂ in the ratio 1 part by volume of the stabilizer concentrate to 199 parts of the 50 volume hydrogen peroxide solution.

The concentrate was made up by dissolving 80 gm of tartaric acid and 21 gm of citric acid in 500 ml de-ionised water at room temperature using a standard laboratory PYREX beaker suitably cleaned with de-ionised water. To this solution there was added 50 gm 85% orthophosphoric acid and the volume was made up to 1000 ml with de-ionised water stirred for one hour until the solution was homogeneous.

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After filtration through a 45µm millipore filter the concentrate solution was added to 50 volume H₂O₂ in the ratio 1 part by volume of the stabilizer concentrate to 199 parts of the 50 volume hydrogen peroxide solution.

Not only does the concentrate solution stabilize the hydrogen peroxide against decomposition into water and oxygen, but the stabilizing solution itself is biodegradable and, furthermore, does not have any adverse characteristics of the type associated with the use of other stabilizers such as hippuric acid and peracetic acid.

It is envisaged that the stabilized hydrogen peroxide solution will find extensive use in various disinfectant applications, the reduction of algae growth, the reduction of aldehydes, phenols, cyanides, sulphides and mercaptans, photo-effluent treatment, the reduction of sulphur and nitrogen oxides, odour removal and chlorine replacements.

The disinfectant product of this example is particularly useful for disinfectant of swimming pools and does not have the disadvantages mentioned above with respect to the use of hypochlorites. It was tested in terms of "Standard Method 682" of The South African Bureau of Standards to measure its efficacy as an algaeicide and bactericide for swimming pool use. The standard requires that no growth of algae should occur within 28 days after inoculation of test samples of the disinfectant solution with algae growth medium and that no growth of bacteria should occur within the first 48 hours after inoculation. Bactericidal activity was tested using 0.1% peptone water as cultivation medium, incubating the bottles at 37°C and using as test organisms a mixture of Escherichia coli SATCC Esc 25; Staphylococcus aureus SATCC Sta 53; and Pseudomonas aureuginos SATCC Pse 2 containing approximately 10 000 bacteria per ml.

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The results of the test using untreated control and the disinfectant solution of Example 1 at concentrations of 10, 20 and 36 mg/litre are set out in Table I

TABLE I

Concentration	ALGAE CONTROL	BACTERIA CONTROL
	No. of days to visible growth of algae	Growth of micro-organisms after 48 hours
Untreated Control	3	Positive
10	11	Positive
20	13	Positive
36	28	Negative

It will be seen that the disinfectant of the invention provided eeffective control of micro-organisms in the standard test using 36mg/litre of the disinfectant solution, i.e. 36 ppm in swimming pool applications. Since use of the disinfectant at 60-80 ppm in swimming pool applications is permitted, the disinfectant solution of Example 1 is shown to be a highly effective swimming pool disinfectant product.

EXAMPLE 2

In the second example of the invention a stabilizing solution for use in stabilizing a 35 volume hydrogen peroxide solution to give a highly effective bactericide is provided.

This stabilizing solution has the following typical composition and characteristics:

pH	0.96
total dissolved solids	195000
specific gravity	1.27
silver nitrate	26.64% mass/volume

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citric acid	2.10% mass/volume
tartaric acid	8.00% mass/volume
phosphoric acid	4.30% mass/volume

The concentrate was made up by dissolving 266.4 gm silver nitrate in 500 ml de-ionised water. The solution was heated to 30°C while stirring and 21 gm citric acid and 80 gm tartaric acid were then added and allowed to dissolve before adding 50 gms of 85% orthophosphoric acid. The solution was made up to 1000ml using de-ionised water and stirred for 2 hours. The solution was then filtered through a 45 µm millipore filter.

After filtration, the stabilizing solution was added to the 35 volume hydrogen peroxide in the ratio of 1 part by volume of the stabilizing solution to 199 parts by mass of the 35 volume hydrogen peroxide solution to provide a disinfectant having from 5 to 10 ppm of the stabilizing agent and about 1000 ppm of silver ions.

The concentrate stabilizes the hydrogen peroxide against decomposition, particularly in the presence of the silver ions and the silver ions provide enhancement of the hydrogen peroxide insofar as its bactericidal properties are concerned. The disinfectant is effective at 0.01 to 0.5% dilution for sanitization of food machinery and surface disinfection in general.

In order to rate the silver-containing disinfectant solution of Example 2 it was compared with three commercially available

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hydrogen peroxide/peracetic acid disinfectant compositions at their recommended use dilutions of:-

Example 2 disinfectant	0.5%
Commercial Disinfectant A	0.4%
Commercial Disinfectant B	0.15%
Commercial Disinfectant C	0.2%

These products were tested against cultures of Bacillus, E. Cloacae, Pepiococcus spp., Lactobacillus spp., Sarcina which were grown in ULM overnight and cultures of 2036 (Yeast), Picia, Candida and S. Ellipsoideus which were grown up in MYGP broth overnight. The grown cultures were then bulked and spun down at 25 000 rpm for 10 minutes. The supernatant was discarded and the pellet re-suspended in 100 ml of saline to make a suspension of approximately 10^6 cells/ml.

The disinfectants were made up to their required concentrations and the amount of caustic required to neutralize 5 ml of each of them was determined. The specific amount of caustic were then measured into bottles and sterilized.

1 ml of the prepared culture was inoculated into 50 ml of each of the disinfectant solutions and after intervals of 5, 10, 15, 20, 25 and 30 minutes 5 ml was removed and immediately neutralized by caustic. 0.2 ml of the neutralized solution was plated onto each of the LMDA and WLN and incubated at 30°C and 25°C respectively whereafter bacterial counts were made.

The results are set out in Table II

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TABLE II

M I N U T E S

	5	10	15	20	25	30
Example 2 (0.5%) LMDA WLN	0	0	0	0	0	0
	0	0	0	0	0	0
Disinfectant A (0.4%) LMDA Bacillus	2 Bacillus	1 Bacillus	2 Bacillus	4 Bacillus	0	2
WLN	0	0	0	0	0	0
Disinfectant B (0.15%) LMDA Bacillus	5 Bacillus	5 Bacillus	6 Bacillus	5 Bacillus	5 Bacillus	5
WLN	0	0	0	0	0	0
Disinfectant C (0.2%) LMDA WLN	300*	300*	200*	200*	100*	100*
	TNTC*	TNTC*	TNTC*	TNTC*	TNTC*	

* = mixed culture

TNTC = too numerous to count

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These results show that with a culture containing approximately 10^6 cells/ml, the disinfectant of Example 2 was the most effective with disinfectants A & B being effective as well. However, disinfectant C did not compare satisfactorily with the other compositions tested.

In order to compare the disinfectant product of Example 2 with a commercial iodophor, brewery fermentation vessels were sterilized using the normal commercial iodophors and the Example 2 product of the invention. Repeated disinfection runs were made using the iodophor and the product of Example 2 separately and the sanitizing effect of the two products was determined by taking swabs from the test vessels and subjecting them to quantitative microbiological analysis. These analyses indicate whether or not the vessel is sterile. A vessel which is sterile is said to be "under control".

The results are set out in Table III from which it will be seen that the disinfectant of the invention provided substantially improved sanitation control of brewery equipment.

TABLE III

MONTH	FREQUENCY	IN CONTROL	% IN CONTROL
September (Iodophor)	163	137	84
October (Iodophor)	122	118	96
October (Example 2)	86	86	100
November (Example 2)	175	172	98

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The product was further compared with a commercial stabilized hypochlorite disinfectant for sanitization of a brewery pasteurizer unit. Repeated disinfection runs were made on the unit after each operation thereof by depositing the test disinfectant in the sump of the unit. In the case of the hypochlorite sufficient product was used to maintain a free chlorine residual < 0.5 ppm while the disinfectant of Example 2 was used to maintain a residual of hydrogen peroxide Of 20 - 50 ppm.

The products were in each case fed continuously to the machine sumps to maintain the required residuals. As an operation standard acceptable bacterial counts were taken to be $< 10^4$ micro-organisms/ml and wild yeasts count at < 10 organisms/ml. Each test was run over a period of 24 hours.

The results are set out in Tables IV and V from which it will be seen that the stabilized hydrogen peroxide disinfectant solution of the invention was superior.

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TABLE IV

Hypochlorite Disinfectant

TEST RUN NO.	MICRO-ORGANISMS COUNT Per ml	WILD YEAST COUNT Per ml
1	TNTC	TNTC
2	94	12
3	TNTC	8
4	TNTC	56
5	TNTC	TNTC
6	TNTC	20
7	800	TNTC
8	TNTC	60
9	TNTC	TNTC
10	TNTC	TNTC
11	TNTC	46

TABLE V

Example 2 Disinfectant

TEST RUN NO.	MICRO-ORGANISMS COUNT Per ml	WILD YEAST COUNT Per ml
1	nil	nil
2	nil	nil
3	10	nil
4	34	nil
5	1	nil
6	4	nil
7	1	nil
8	5	nil
9	63	nil
10	6	nil
11	56	nil
12	nil	nil
13*	64	8
14	6	nil
15	89	nil
16	95	12
17	10	10

* = feed to sump 1 interrupted for 12 hours
 TNTC = too numerous to count

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Example 3

Stabilized hydrogen peroxide disinfectant solution containing a quaternary ammonium salt.

The disinfectant solution produced in terms of Example 1 was used and 5 mass % by volume of BELLACIDE 350 was added thereto.

The resulting disinfectant solution is particularly suitable for use in the disinfectant of brewery equipment. In order to compare the disinfectant solutions of Examples 1 to 3 tests were run on brewery pasteurizers for slime control using the three products.

In each case the products were fed into the sumps of brewery pasteurizers to maintain machine residual of 20 to 50 ppm of hydrogen peroxide and the disinfectant was distributed through the machines using the normal circulating pumps.

The pasteurizers were run for a period of 4 days and visual inspections were made at 24-hour intervals. The pasteurizer using the disinfectant product of Example 1 developed fairly heavy slime after 48 hours indicating the growth of micro-organisms in excess of 10^6 organisms/ml. The pasteurizing equipment using the silver-containing disinfectant solution of Example 2 provided an operationally clean machine indicating that the disinfectant was effective to control micro-organisms to provide a count of less than 10^4 organisms/ml.

The pasteurizing equipment using the product of Example 3 was even cleaner than that using the disinfectant of Example 2 on visual inspection after 4 days.

Thus the disinfectant product of Example 3 is at least as effective as that of Example 2 containing silver ions.

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Example 4

Dilute stabilized hydrogen peroxide solution with ultra-violet blocker.

In order to test the efficacy of acetanilide to prevent degradation of the hydrogen peroxide solution, samples were prepared according to Example 1 at 0.05% and acetanilide was added to some of the samples which were then irradiated using a 40w ultra-violet light source suspended in a cabinet about 20 cm. above the samples.

The irradiation was continuous over a period of 24 hours and two different sources of commercial 50% volume hydrogen peroxide were utilized.

The results of the test are set out in Table VI.

TABLE VI

ULTRA-VIOLET STABILITY OF DILUTE H₂O₂ SOLUTIONS

	Sample	Initial H ₂ O ₂ Conc. (ppm)	Final H ₂ O ₂ Conc. (ppm)	% H ₂ O ₂ loss Conc.	Remarks
	Control A	530	528	0.4	Samples kept in dark for 24 hrs.
	Control B	525	514	0.2	
Set 1	Sample A	461	402	15.5	containing no acetanilide
	Sample B	509	47	16.1	
Set 2	Sample A	551	473	14.2	+ 1 ppm acetanilide
	Sample B	546	496	9.0	
	Sample A	472	429	9.0	+ 5 ppm acetanilide
	B	512	506	1.0	

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Table VI illustrates the effectiveness of acetanilide but also shows that the source of hydrogen peroxide plays an important role.

Initial tests have further indicated that not only do the stabilizing solutions stabilize the hydrogen peroxide against rapid decomposition into water and oxygen, but the stabilizing solution themselves, especially the silver-free embodiments, are biodegradable and, furthermore, do not have any adverse characteristics of the type associated with the use of other stabilizers or inhibitors such as hippuric acid, acetanilide, orthophosphoric acid and peracetic acid.

It is envisaged that the stabilized hydrogen peroxide solution will find extensive use in various disinfectant applications, the reduction of algae growth, the reduction of aldehydes, phenols, cyanides, sulphides and mercaptans, photo-effluent treatment, the reduction of sulphur and nitrogen oxides, odour removal and chlorine replacements.

The resultant solution desirably contains approximately 700 ppm of the stabilizing agent and (if used) about 1000 ppm of silver ions.

It will readily be appreciated that the stabilizing agent stabilizes the hydrogen peroxide against decomposition. In the embodiments characterised by the presence of silver ions, the silver ions constitute an enhancement of the hydrogen peroxide solution insofar as its bactericidal properties are concerned.

It is particularly envisaged that the resultant solutions according to the invention (especially the silver-free embodiments) will be used as disinfectants and biocides even to the extent of disinfecting potable water and other water sources such as swimming pools for example.

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Stabilized hydrogen peroxide solutions produced in accordance with Example 1 and Example 2 were used as biocidal agents in swimming pools at various concentrations and the results are shown in the following Table.

TABLE VII

RESULTS

Product	Concentration p.p.m.	Number of days to visible growth of algae	Growth of bacteria after 48 h
Untreated control	0	3	Positive
Example 1	60	14	Negative
	80	20	Negative
	100	23	Negative
Example 2	10	4	Positive
	20	7	Positive
	35	12	Negative
Example 2*	10	6	Positive
	20	12	Positive
	35	20	Negative

*53.28% mass volume silver nitrate

It can be seen from the above Table that the composition of Example 1 was effective in eliminating bacterial growth after 48 hours at each of the three concentrations used whereas for the silver-containing compositions of Example 2, bacterial growth was inhibited only at the highest concentration. However at this concentration, the level of silver was excessively high to enable the composition to be used as a swimming pool disinfectant, in view of its deleterious effects on rubber and plastic swimming pool fittings. That the composition of Example 1 had a complete inhibitory effect at each of the concentrations tested and furthermore inhibited algae growth for a substantial period of time was particularly surprising as such properties of a disinfectant composition containing hydrogen peroxide as the sole disinfecting agent and

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in the substantial absence of silver had not been suspected hitherto.

EXAMPLE 5

Stabilized hydrogen peroxide solutions were prepared as follows:

- A - according to Example 1
- B - according to Example 2
- C - according to Example 1 of GB-A-2 189 394
- D - commercially available product (ADDOX)

The resulting solutions were assessed for their disinfectant ability by testing their biocidal activity against four test organisms. The results are given in the following Tables VIII, IX, X and XI.

The superiority of the compositions of the invention is apparent.

TABLE A - ACCORDING TO EXAMPLE 1

(DESTRUCTION RATES IN PERCENT)

	15 MINUTES		30 MINUTES		60 MINUTES	
	20°C	40°C	20°C	40°C	20°C	40°C
30ppm						
E. coli	12.4	21.3	-	25.8	37.3	62.6
S. aureus	7.2	-	21.8	62.2	39.7	59.4
P. aeruginosa	27.2	73.0	47.3	89.4	44.1	97.9
C. albicans	-	76.1	-	87.1	-	98.5
75ppm						
E. coli	29.8	8.6	21.8	34.5	38.7	65.3
S. aureus	21.1	37.3	23.1	74.3	32.3	89.7
P. aeruginosa	24.9	84.5	72.2	97.7	78.1	99.8
C. albicans	-	87.2	-	99.2	3.5	99.9

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TABLE B - ACCORDING TO EXAMPLE 2

(DESTRUCTION RATES IN PERCENT)

	15 MINUTES		30 MINUTES		60 MINUTES	
	20°C	40°C	20°C	40°C	20°C	40°C
30ppm						
<i>E. coli</i>	-	38.9	11.3	50.2	18.6	91.72
<i>S. aureus</i>	12.3	-	9.3	93.5	23.2	99.7
<i>P. aeruginosa</i>	13.5	85.3	17.4	99.9	22.0	99.9
<i>C. albicans</i>	18.2	48.0	14.0	83.7	39.7	99.9
75ppm						
<i>E. coli</i>	17.5	42.4	13.5	75.8	85.3	98.8
<i>S. aureus</i>	2.82	24.9	14.5	41.9	17.3	100
<i>P. aeruginosa</i>	-	99.0	31.1	100	92.8	100
<i>C. albicans</i>	43.4	99.9	52.6	100	93.1	100

TABLE C - ACCORDING TO EXAMPLE 1 OF GB-A-2 189 394

(DESTRUCTION RATES IN PERCENT)

	15 MINUTES	30 MINUTES	60 MINUTES	90 MINUTES	120 MINUTES
10ppm					
E. coli	-	-	-	40.0	31.8
K. pneumoniae	-	28.9	-	35.0	35.3
20ppm					
E. coli	-	-	17.6	30.0	40.9
K. pneumoniae	4.6	39.1	15.9	38.0	45.0
30ppm					
E. coli	-	13.3	29.4	35.0	54.5
K. pneumoniae	20.7	33.0	14.8	40.0	55.6

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TABLE D
-
COMMERCIALY AVAILABLE PRODUCT (ADDOX)

TEST GERM	Count per ml	TEST CONCENTRATION %										Value (Sterile Water)
		10	1	0.1	0.05	0.01	0.0075	0.005	0.002	0.001	0.0005	
E.Coli	53x10 ⁶	-	-	-	-	-	-	-	-	-	(+)	++
K.Pneumoniae	6.1x10 ⁶	-	-	-	-	-	-	-	-	-	+	++
S.aureus	50x10 ⁶	-	-	-	-	-	-	-	-	-	-	++
S.faecalis	36x10 ⁶	-	-	-	-	-	-	-	-	-	(+)	++
P.mirabilis	24x10 ⁶	-	-	-	-	-	-	-	-	-	-	++
S.sporogeres	2.1x10 ⁶	-	-	-	-	-	-	-	-	++	++	++

Explanation of symbols

- = No growth
 (+) = Slight growth
 + = Evident growth
 ++ = Strong growth

For each preparation a growth control test was carried out under the same experimental conditions but without the addition of A D O X. All the germs tested showed strong growth in the control test.

SUBSTITUTE SHEET

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CLAIMS

1. An aqueous stabilizing solutions for stabilizing hydrogen peroxide, comprising the following constituents

Citric acid	1 to 7 weight percent
Tartaric acid	7 to 12 weight percent

and a chelating and/or buffering agent.

2. An aqueous stabilizing solution according to Claim 1 said chelating and/or buffering agent being in a sufficient concentration to effect substantially complete chelation of metal ions capable of catalyzing the decomposition of hydrogen peroxide.

3. An aqueous stabilizing solution according to Claim 1 or Claim 2 additionally comprising silver ions in the concentration range of 5 to 30 mass % .

4. An aqueous stabilizing solution according to Claim 3 wherein said silver ions are provided in the form of a soluble silver salt such as at least one of silver nitrate, silver sulphate and silver nitrite, or as silver chloride.

5. An aqueous stabilising solution according to claim 4 in which the silver ions are incorporated into the solution as silver nitrate and the ratio of silver nitrate to citric acid to tartaric acid to phosphoric acid is 13:1:4:2.

6. An aqueous stabilizing solutions for stabilizing hydrogen peroxide, comprising the following constituents

Citric acid	1 to 7 weight percent
Tartaric acid	7 to 12 weight percent

and a chelating and/or buffering agent said compositions being further characterized by the substantial absence of silver.

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7. An aqueous stabilizing solution according to any preceding claim wherein the chelating and/or buffering agent is present in a proportion of 2 to 6 parts (mass % volume).

8. An aqueous stabilizing solution according to any preceding claim wherein the chelating and/or buffering agent comprises phosphate ions.

9. An aqueous stabilizing solution according to any preceding claim wherein the phosphate ions are provided by incorporating phosphoric acid into the composition, preferably in a concentration in the range of from 2 to 6 weight percent.

10. An aqueous stabilizing solution according to any preceding claim having a pH of the stabilizing solution in the range of from 1.5 to 3.

11. An aqueous stabilizing solution according to any preceding claim including the following constituents in the ratio indicated:

Citric acid:tartaric acid:phosphoric acid = 1:4:2

12. An aqueous stabilizing solution according to my preceding claim wherein said constituents are dissolved in demineralised water.

13. An aqueous stabilising solution according to any preceding claim in which the citric, tartaric and phosphoric acids are provided in the ratio 1:4:2 respectively, the concentrate having a pH of 1.5 to 3 and a maximum dissolved solids content of 38 000 ppm.

14. An aqueous stabilising solution according to any preceding claim including an ultra-violet ray blocking agent.

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15. An aqueous stabilising solution according to Claim 14 in which the ultra-violet ray blocking agent is acetanilide which is included in the range 0.02 to 0.1 mass % by volume.

16. A hydrogen peroxide-containing composition stabilized by the presence of the components of the stabilizing compositions defined in any of Claims 1 to 15.

17. A hydrogen peroxide-containing composition according to Claim 16 prepared by mixing aqueous hydrogen peroxide with the aforementioned stabilizing solutions in the following concentration ratios:

Hydrogen peroxide	99.7 to 97 mass percent/vol.
Stabilizing solution	0.25 to 3.0 mass percent/vol.

18. A hydrogen peroxide-containing composition according to Claim 17 in which the hydrogen peroxide and concentrate are mixed in the ratio 1 to 99 to 1 to 199.

19. A hydrogen peroxide-containing composition stabilized by the presence of the following constituents

Citric acid	0.0025 - 0.21 weight percent
Tartaric acid	0.0175 - 0.36 weight percent

and a chelating agent for chelating metal ions.

20. A hydrogen peroxide-containing composition according to any of Claims 16 to 19 said composition being further characterized by the substantial absence of silver.

21. A hydrogen peroxide containing composition according to any of Claims 16 to 20 including a phase transfer agent.

22. A hydrogen peroxide containing composition according to Claims 21 wherein said phase transfer agent comprises a lipid soluble quaternary ammonium salt in the range 5 to 20 mass % by volume.

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23. A hydrogen peroxide-containing composition according to Claim 22 in which the lipid soluble quaternary ammonium salt is BELLACIDE 350.

24. The use of a hydrogen peroxide-containing composition according to any of Claims 16 to 23 as a disinfectant for water.

25. The use according to Claim 24 of one of said hydrogen peroxide-containing compositions as a swimming pool disinfectant.

26. A method of disinfecting a swimming pool or Jacuzzi which comprises periodically adding a biocidally effective amount of a a hydrogen peroxide-containing composition according to Claim 16 to 23.

27. A method of surface disinfection of brewery equipment in which a hydrogen peroxide disinfectant according to any of Claims 16 to 23 is applied to such equipment at effective concentration up to 0.5 mass % by volume.

28. A method of producing a silver-containing stabilizing solution for stabilizing hydrogen peroxide which comprises the following steps carried out in the order specified:

A. forming an aqueous solution comprising a water soluble silver salt at a temperature of from 20 to 40°C

B. forming an aqueous solution comprising a water soluble silver salt, tartaric acid and citric acid from the solution formed in Step A

C. forming an aqueous solution comprising a water soluble silver salt, tartaric acid, citric acid, and phosphoric acid from the solution formed in Step B

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29. A method according to Claim 28 wherein in carrying out Step B, solid citric acid and tartaric acid is be dissolved in the solution formed in Step A.

30. A method according to Claim 28 wherein in carrying out Step B, citric acid and tartaric acid dissolved in water are mixed with the solution formed in Step A.

31. A method according to any of Claims 28 to 30 wherein in Step C the solution from Step B is mixed with aqueous phosphoric acid.



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁵ : C01B 15/037, A01N 59/00 C02F 1/00, 1/72	A3	(11) International Publication Number: WO 91/0898 (43) International Publication Date: 27 June 1991 (27.06.91)
(21) International Application Number: PCT/GB90/01968 (22) International Filing Date: 17 December 1990 (17.12.90) (30) Priority data: 89/9597 15 December 1989 (15.12.89) ZA (71) Applicant (for all designated States except US): AQUAC- LEAR INTERNATIONAL LIMITED [GB/GB]; 30 Aylesbury Street, London EC1R 0ER (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : KELLY, Felix [GB/ GB]; 16 Bramley Grove, Crowthorne, Berkshire RG11 6EB (GB). McKAY, Colin [GB/ZA]; 20 Oakhill, Steen- braas Street, Gallo Manor, Johannesburg (ZA). STEED, Brian, Harold [GB/ZA]; 6 Elm Road, River Club, Jo- hannesburg (ZA).		(74) Agent: RITTER, Stephen, David; Mathys & Squire, 1 Fleet Street, London EC4Y 1AY (GB). (81) Designated States: AT, AT (European patent), AU, BB, BI (European patent), BF (OAPI patent), BG, BJ (OAP patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE DE (European patent), DK, DK (European patent), ES ES (European patent), FI, FR (European patent), G/ (OAPI patent), GB, GB (European patent), GR (Eurc pean patent), HU, IT (European patent), JP, KP, KR LK, LU, LU (European patent), MC, MG, ML (OAP patent), MR (OAPI patent), MW, NL, NL (Europea patent), NO, RO, SD, SE, SE (European patent), ST (OAPI patent), SU, TD (OAPI patent), TG (OAPI pa tent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending th</i> <i>claims and to be republished in the event of the receipt o</i> <i>amendments.</i> (88) Date of publication of the international search report: 5 September 1991 (05.09.91)

(54) Title: SOLUTIONS FOR STABILIZING HYDROGEN PEROXIDE CONTAINING SOLUTIONS

(57) Abstract

Aqueous stabilizing solutions are provided for stabilizing hydrogen peroxide, comprising the following constituents: citric acid 1 to 7 mass percent/vol., tartaric acid 7 to 12 mass percent/vol. and a chelating and/or buffering agent. In one set of embodiments, the stabilizing solution may include silver ions in the concentration range 5 to 30 parts mass % by volume. Other embodiments of the invention are characterized by the substantial absence of silver. The stabilizing compositions may be used to stabilize hydrogen peroxide-containing composition useful as a disinfectant for water, e.g. as a swimming pool disinfectant.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01968

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁴ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 01 B 15/037, A 01 N 59/00, C 02 F 1/00, C 02 F 1/72											
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border: 1px solid black; padding: 5px;">Classification System</th> <th style="border: 1px solid black; padding: 5px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 10px; vertical-align: top;">IPC⁵</td> <td style="border: 1px solid black; padding: 10px; vertical-align: top;">C 01 B, A 01 N, C 02 F</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁵	C 01 B, A 01 N, C 02 F					
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IPC ⁵	C 01 B, A 01 N, C 02 F										
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border: 1px solid black; padding: 5px;">Category ⁹</th> <th style="width: 70%; border: 1px solid black; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border: 1px solid black; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border: 1px solid black; padding: 10px; vertical-align: top; text-align: center;">A</td> <td style="border: 1px solid black; padding: 10px; vertical-align: top;">GB, A, 2189394 (SANOSIL AG) 28 October 1987 cited in the application --</td> <td style="border: 1px solid black;"></td> </tr> <tr> <td style="border: 1px solid black; padding: 10px; vertical-align: top; text-align: center;">A</td> <td style="border: 1px solid black; padding: 10px; vertical-align: top;">Chemical ABstracts, vol. 105, no. 2, 14 July 1986, (Columbus, Ohio, US), see page 261, abstract 10545g, & AU, B, 546214 (METROP. WATER SEWERAGE & DRAIN. BOARD) 22 August 1985 -----</td> <td style="border: 1px solid black;"></td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	GB, A, 2189394 (SANOSIL AG) 28 October 1987 cited in the application --		A	Chemical ABstracts, vol. 105, no. 2, 14 July 1986, (Columbus, Ohio, US), see page 261, abstract 10545g, & AU, B, 546214 (METROP. WATER SEWERAGE & DRAIN. BOARD) 22 August 1985 -----	
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IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">19th June 1991</div> </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold;">06.08.91</div> </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;"> miss T. MORTENSEN </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">19th June 1991</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold;">06.08.91</div>	International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;"> miss T. MORTENSEN </div>					
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FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE :

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING :

This International Searching Authority found multiple inventions in this international application as follows:

1. Claims 1-18, 20-27 in so far as not linked to claim 19, on condition that 18 is corrected, 28-31
2. Claims 19, 20-27 in so far as linked to claim 19, on condition that 18 is corrected
1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☒ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9001968

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 18/07/91
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2189394	28-10-87	CH-A- 673225	28-02-90
		AT-B- 389802	12-02-90
		AU-B- 590379	02-11-89
		AU-A- 6785487	29-10-87
		BE-A- 1000083	02-02-88
		DE-A- 3620609	05-11-87
		FR-A- 2597347	23-10-87
		JP-A- 62255401	07-11-87
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